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Sensitivity of hazardous air pollutant emissions to the combustion of blends of petroleum diesel and biodiesel fuel

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ABSTRACT

Emission rates and composition of known hazardous air pollutants in the exhaust gas from a commercial agriculture tractor, burning a range of biodiesel blends operating at two different load conditions were investigated to better understand the emission characteristics of biodiesel fuel. Ultra-Low Sulfur Petroleum Diesel (ULSD) fuel was blended with soybean oil and beef tallow based biodiesel to examine fuels containing 0% (B0), 50% (B50) and 100% (B100) soybean oil based biodiesel, and 50% (B50T) and 100% (B100T) beef tallow biodiesel. Samples were collected using a dilution source sampler to simulate atmospheric dilution. Particulate matter and exhaust gases were analyzed for carbonyls, Volatile Organic Compounds (VOCs), and Polycyclic Aromatic Hydrocarbons (PAHs) to determine their respective emission rates. This analysis is focused on the emissions of organic compounds classified by the US EPA as air toxics and include 2,2,4 trimethylpentane, benzene, toluene, ethylbenzene, *m*-, *p*- and *o*-xylene, formaldehyde, acetaldehyde and methylethyl ketone. Emission rates of 2,2,4 trimethylpentane, toluene, ethylbenzene, *m*-, *p*- and *o*-xylene decreased more than 90% for B50, B100 and B100T blends; decreases in emission rates of benzene, formaldehyde and acetaldehyde were more modest, producing values between 23 and 67%, and methyl ethyl ketone showed decreases not exceeding 7% for the studied biodiesel blends. PAHs emission rates were reduced by 66% for B50, 84% for B100, and by 89% for B100T. The overall emissions of toxic organic compounds were calculated and expressed as benzene equivalents. The largest contributors of toxic risk were found to be formaldehyde and acetaldehyde. Reductions in formaldehyde emissions were 23% for B50 and 42% for B100 soybean, and 40% for B100T beef tallow compared to B0. Similarly, acetaldehyde reductions were 34% for B50 and 53% for B100 soybean biodiesel and 42% for B100T beef tallow biodiesel.

1. Introduction

Human and animal studies suggest that diesel exhaust is a likely carcinogen (McClellan, 1986; Valberg and Watson, 1996; Nilsen et al., 1999; Mauderly, 2001; Hesterberg et al., 2006; Ris, 2007). Human epidemiological studies demonstrate an association between diesel exhaust exposure and increased lung cancer rates in occupational settings (USEPA, 2002). Although there is limited information regarding health effects related to exposure to specific components of diesel exhaust, a subset of these components are included in the US EPA list of hazardous air pollutants, such as acetaldehyde, formaldehyde and other carbonyl species, benzene, toluenes, xylenes and polycyclic organic matter. The EPA definition of the nonroad engine is based on the principle of mobility/portability, and includes engines installed on (1) self-propelled equipment, (2) on equipment that is propelled while performing its function, or (3) on equipment that is portable or transportable, as indicated by the presence of wheels, skids, carrying handles, dolly, trailer, or platform. In other words, nonroad engines are all internal combustion engines except motor vehicle (highway) engines, stationary engines (or engines that remain at one location for more than 12 months), engines used solely for competition, or engines used in aircraft (USEPA, 2003).

Several studies have detailed emission rates of volatile organic compounds (VOCs), carbonyls and PAHs found in diesel exhaust of onroad medium-duty vehicles (Schauer et al., 1999), and heavy-duty engines with exhaust after-treatment control technologies

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(Liu et al., 2010). The fast spread of biodiesel usage around the globe, has led to special interest in the effects these fuels could have on diesel engine emissions, and subsequent human health and climate change impacts (Morris and Jia, 2003). Recent studies have shown increases in carbonyl emissions from onroad heavy-duty diesel engines without exhaust after-treatment control operating with blends of petroleum diesel fuel with vegetable and animal origin biodiesel (Correa and Arbilla, 2008; He et al., 2009; Ballesteros et al., 2011). Other studies have found decreases in carbonyl emissions for the same type of engines operating on biodiesel blends (Guarieiro et al., 2008; Peng et al., 2008; Lin et al., 2009; Yuan et al., 2009). In addition, after-treatment controls have been found to produce decreases in such emissions (Ballesteros et al., 2011). Driving cycles, after-treatment controls, and the origin of the biodiesel fuel used clearly affect the impact of biodiesel blends on carbonyl emissions from onroad heavy-duty diesel vehicles (Fontaras et al., 2010). Estimates of biodiesel's effect on PAH emissions from onroad diesel engines are contradictory, since some studies have shown increases in PAH emissions attributed to biodiesel blends (Karavalakis et al., 2011; Lin et al., 2011), while others have found the opposite effect (Yang et al., 2007; He et al., 2010; Lin et al., 2011). With respect to VOC emissions, engines operating on biodiesel have shown consistent reductions in emissions (Ballesteros et al., 2008; Ferreira et al., 2008; Payri et al., 2009).

Only limited investigation of emissions of air toxics from nonroad vehicles has been conducted, even though nonroad engines are major contributors to nationwide cancer risk from air toxic pollutants (EPA, 2002). To address this knowledge gap, this study specifically examines the toxic emissions from a nonroad diesel vehicle. Furthermore, rather than focusing on a single chemical class of compounds, this study seeks to present a more comprehensive view of the impact of biodiesel on emissions of air toxics as a whole.

2. Materials and methods

2.1. Testing vehicle, fuel blends, and additional equipment

The vehicle used for this study was a 1993 John Deere model 7700 agricultural tractor operated without any exhaust after-treatment control device. This model is commonly used with pure petroleum diesel fuel, and with commercial and home-made biodiesel blends. The engine load was controlled with a Power Take Off (PTO) dynamometer AW NEB-400 in two specific modes: Idle, for 10 min; followed by operations at the manufacturers rated speed of 2100 RPM and 126.08 HP, for twenty minutes. Samples were collected after the whole testing time of 30 min. The driving cycle used for the emissions test was selected to best mimic real world operating conditions of agricultural tractors that are used to power farming activities, based on discussions with John Deere experts at the Madison Area Technical College (MATC). The fuels used for the study were commercially available Ultra Low Sulfur Diesel fuel (ULSD, B0), virgin soybean oil based biodiesel (Chevron Philips Chemical Company, The Woodlands TX) and beef tallow based biodiesel (Nova Biofuels Seneca, Seneca IL). Blends of petroleum diesel fuel with soybean biodiesel (25% (B25), 50% (B50), 75% (B75) and 100% (B100) by volume), and with beef tallow biodiesel (100% (B100T) by volume) were tested. Three tests were performed for each of the soybean biodiesel blends and two tests were performed for the tallow biodiesel blend. Four dynamic and one loading blank tests were performed to assess data quality and control. Dynamic blank tests consist of a regular 30 min test with no exhaust coming into the sampler; the purpose of these tests is to establish the level of contamination in the sampler and by the filtered and activated carbon scrubbed dilution air. Loading blank tests consist of loading all sampling media and collecting them after several minutes in order to estimate the level of contamination introduced by sample handling.

2.2. Sampling procedure

The engine exhaust was diluted in a dilution stack sampler with filtered and scrubbed ambient air, to mimic real atmospheric dilution of engine exhaust. This sampler is described by Hildemann (Hildemann et al., 1989) and operated in a similar setting to Okuda (Okuda et al., 2009). Particle phase PAHs were analyzed from quartz fiber filters (QFF) (Pall Life Sciences, Ann Arbor MI), supported by aluminum holders, after a $PM_{2.5}$ cyclone to remove coarse particles at a flow rate of 12 L per minute (LPM). Gas phase PAHs were collected in a cartridge with two pre-cleaned Polyurethane Foam (PUF) plugs (Sigma–Aldrich Inc., St Louis MO), separated by a layer of XAD resin (Supelco, Rohm & Haas Amberlite XAD®2, Sigma–Aldrich Inc., St Louis MO), after a QFF and a $PM_{2.5}$ cyclone to remove particles. Samples were collected at a flow rate of 24 LPM following the sampling methodology used by Schauer (Schauer et al., 1999). Semivolatile/volatile carbonyl species were collected by Sep-Pak®DNPH-Silica cartridges (Waters Corporation, Milford, MA) at a constant flow rate of 1 LPM. VOC species were collected in 6L SUMMA® canisters at a flow rate of 0.2 LPM as described by Schauer (Schauer et al., 1999). Supplemental Figure S2 shows a schematic of the different sampling trains connected to the dilution stack sampler used in this study.

2.3. Analytical techniques

Chemical speciation of particle and gas phase PAHs was performed by Gas Chromatography/Mass Spectrometry (GC/MS) analysis (Sheesley et al., 2004). Particle analysis from composite samples of two or three half filters, depending on the number of tests performed for each test, were spiked with isotopically labeled standard solutions and extracted with 50/50 dichloromethane and acetone solvents using sonication, rotary evaporators and nitrogen evaporators; 250 μL aliquots were used for quantification of PAHs. The reported emission rates were dynamic blank subtracted, and the uncertainty was calculated by taking the square root of the sum of the squared standard deviation of the dynamic blanks plus 20% of each detected value as determined by GCMS analysis (Stone et al., 2008). Gas phase PAH species collected in PUF cartridges were extracted following a similar procedure as explained above. DNPH coated cartridges were desorbed with acetonitrile and analyzed using High Performance Liquid Chromatography with a NOVA-PAK C18 column and UV detection, following the Wisconsin Occupational Health Laboratory (WOHL) method WL051.9 based on EPA method TO11. Non methane organic gases collected in SUMMA canisters were analyzed and speciated by Gas Chromatography/Flame Ionization Detector (GC/FID) following EPA method TO14.

2.4. Emission rates

Emission rates of speciated chemical species were calculated in mass per kilogram of CO_2 in the exhaust gas. Tests for soybean biodiesel blends were performed in triplicate, and in duplicate for the tallow biodiesel blends, which is the basis for the average measurements and uncertainties shown in the results of this study. These measurements were compared with pure ULSD fuel, referred to as B0. Real time measurements of CO_2, O_2, CO, NO, and NO_2 concentrations in the exhaust and in the diluted sample were taken by a TESTO 350 (Testo 350, Testo Inc. US, Sparta, NJ) emission analyzer. Dilution ratios were calculated by comparing

concentrations of CO, NO, and NO_2 in direct exhaust with the diluted sample exhaust. Dilution ratio inside the dilution chamber was determined by dividing the raw exhaust gas concentration by the dilution chamber gas concentration as measured by the portable emissions analyzer. Pollutant concentrations that had the best data quality based on detection limit and repeatability were selected to calculate the dilution ratio for each test. In most tests, NO concentrations showed better data. Dilution ratios calculated for each test can be found in Supplemental Table S1.

3. Results

3.1. Volatile organic compound (VOC) emissions

Of the 34 hydrocarbon species detected by GC/FID in the SUMMA canisters, 8 are included in EPA's Hazardous Air Pollutants (HAP) List (EPA, 2005). 1,3 − Butadiene has been included in Table 1 given its importance as an air toxic, although emission rates of this compound were under detection limits. Fifteen carbonyl species were quantified, but only acetaldehyde, formaldehyde and methylethyl ketone were detected; emissions rates of these species for the different fuel blends included in this study are shown in Fig. 3. These species are all included in the HAP list as well. Table 1 summarizes the ranges of emission rates, inhalation unit risks (OEHHA, 2007) for selected species, sampling media, and analysis technique used for determination of compounds considered for risk analysis. Fig. 1 shows the calculated reductions in emissions of each organic functional group corresponding to the biodiesel blends as compared to B0 fuel. Alkanes, alkenes and aromatics showed similar trends with greater reductions in emission rates for B100 and B100T. Reductions in emissions of alkanes were about 40% for B50, 80% for B100, and 100% for B100T; emission rates of aromatics were reduced by 80% for B50, 95% for B100 and 98% for B100T. Supplemental Table S3 shows detailed emission rates of all analyzed HAPs for each fuel blend. These results show good agreement with previous studies (Ferreira et al., 2008). Nevertheless, other recent studies have shown different results indicating that the variation of carbonyl emissions of biodiesel-fueled engines can be affected by several factors, such as test engine level, biodiesel component and test cycle (He et al., 2009). Correa et al. attributes the increasing emissions of carbonyls with increasing biodiesel content in fuel blends to the ester group in biodiesel fuel (Correa and Arbilla, 2008), whereas Peng et al. attributes reductions in carbonyl emissions with increasing content of biodiesel in fuel blends to its higher oxygen content which can promote complete combustion (Peng et al., 2008).

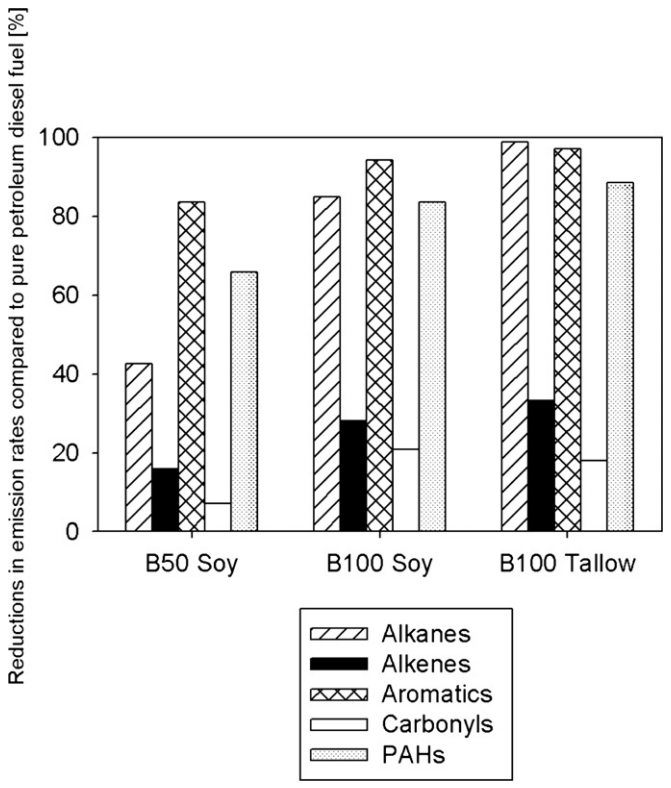

Fig. 1. Reduction in emissions of organic species groups achieved by blending petroleum diesel with soybean oil and beef tallow based biodiesel in an agricultural tractor without exhaust after-treatment devices.

On the other hand, reductions in carbonyl species emissions using B50, B100 and B100T fuels were not greater than 20% compared to B0 as seen in Fig. 3. Fig. 2 shows emission rates of HAP species; toluene and *m*- and *p*-xylenes were the species with higher emissions from B0 fuel and with the highest reductions for B50, B100 and B100T fuels (near 99%). Reductions in benzene emission rates were of 54% for B50 and 50% for B100, and 67% for B100T compared to B0. Formaldehyde emissions were dominant compared to other carbonyl species; they showed decreases of 23% for B50, 42% for B100 and 40% for B100T compared to B0. Acetaldehyde emissions were reduced by 34% for B50, 53% for B100 and 42% for B100T compared to B0. Emission rates of methylethyl ketone did not show significant reductions for blends of biodiesel fuel. Reductions in HAP emissions achieved through the use of biodiesel blends shown very similar numbers for both soybean oil and beef tallow based biodiesel, with the exception of 2,2,4 trimethylpentane and benzene, for which reductions in emission rates using tallow biodiesel were 30 and 15% higher respectively. Nevertheless, the uncertainty associated with measuring emission rates of 2,2,4 trimethylpentane when using tallow biodiesel was considerably higher than for soybean biodiesel. For the rest of the analyzed HAP species the difference in reductions in emission rates associated with the use of soybean or tallow biodiesel was not higher than 9%.

Table 1
Emission rates of analyzed compounds included in the US EPA Hazardous Air Pollutants List present in the exhaust of an agricultural tractor without after-treatment devices operating on petroleum diesel fuel and biodiesel blends with their respective inhalation unit risk values.

Species	Inhalation unit risk $(\mu g\ m^{-3})^{-1}$	Range of emission rates measured (mg kg^{-1} CO_2)
2,2,4-Trimethylpentane	na	0.12–17
Styrene	na	0.11–1
1,3-Butadiene	1.70*E*-04	<0.12
Benzene	2.90*E*-05	4–12
Toluene	na	0.11–60
Ethylbenzene	2.50*E*-06	0.11–10
m and *p*-Xylene	na	0.11–31
o-Xylene	na	0.11–13
Formaldehyde	6.00*E*-06	60–115
Acetaldehyde	2.70*E*-06	15–30
Acrolein	na	<12
Propionaldehyde	na	<30
Methyl Ethyl Ketone	na	15–18

na: Values not available in OEHHA/ARB Risk Assessment Values list.
Samples of hydrocarbon gases were collected in SUMMA canister and analyzed by GC/FID (Gas Chromatography/Flame Ionization Detector).
Samples of carbonyl gases were collected in DNPH (Dinitrophenylhydrazine) cartridges and analyzed by HPLC (High Performance Liquid Chromatography). See text for details.

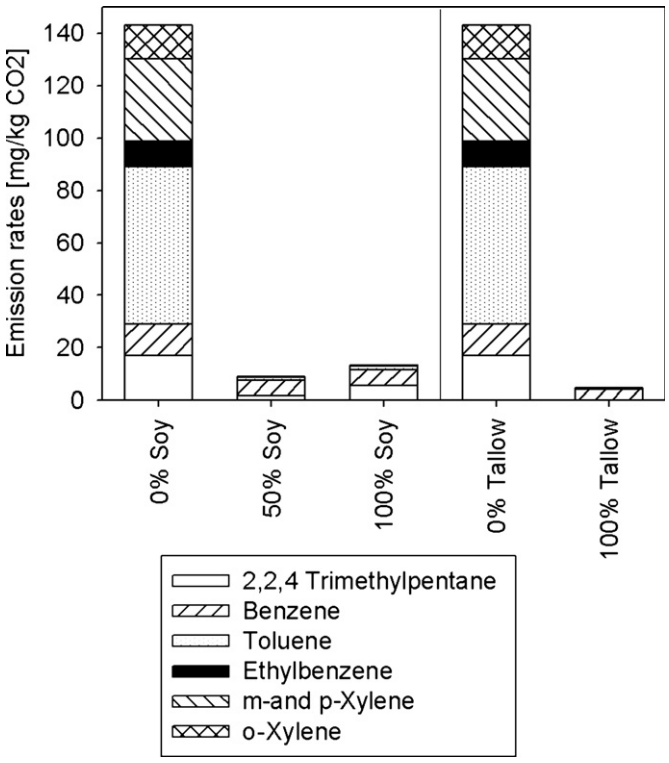

Fig. 2. Emission rates of analyzed hydrocarbon species included in the US EPA hazardous air pollutants list for different blends of petroleum diesel fuel and soybean oil and beef tallow based biodiesel in an agricultural tractor without exhaust after-treatment devices.

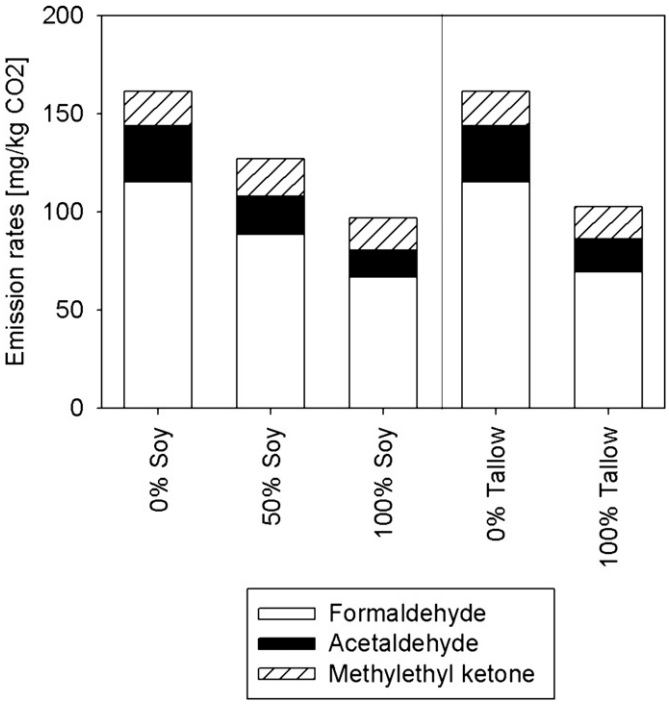

Fig. 3. Emission rates of analyzed carbonyl species included in the US EPA hazardous air pollutants list for different blends of petroleum diesel fuel and soybean oil and beef tallow based biodiesel in an agricultural tractor without exhaust after-treatment devices.

3.2. Gas and particle phase PAHs emissions

Reductions in emission rates of PAHs shown in Fig. 1 account for total emissions, including both particle and gas phase species. Table 2 summarizes ranges of emission rates, inhalation unit risks (OEHHA, 2007) for selected species, sampling media, and analysis technique used for determination of PAHs. From the total 19 PAH species analyzed, only emission rates of 6 of them exceeded detection limits. As seen in Fig. 1, total PAH emission rates reductions were about 65% for B50, 84% for B100, and 89% for B100T. The decrease in PAH emissions for biodiesel blends found in this study show agreement with previous studies on emissions of palm oil based biodiesel (Lin et al., 2006) and soybean oil based biodiesel (Tsai et al., 2010). Fig. 4 show phenanthrene emissions as dominant compared with the other detected species. Reductions in phenanthrene, anthracene, and pyrene emissions ranged between 60 and 75% for B50, 80–90% for B100, and 85–95% for B100T compared to B0. Emissions of fluoranthene and benzo(ghi)fluoranthene showed lower reductions with values varying between 10 and 30% for B50, 30–45% for B100, and 35–60% for B100T compared to B0. Gas phase emissions of low molecular weight (LMW) PAHs phenanthrene and anthracene are dominant compared to particle emissions. On the other hand, particle emissions of high molecular weight (HMW) PAH species fluoranthene, pyrene and Benzo(ghi)fluoranthene dominate, compared to gas emissions.

3.3. Toxic organic compound emissions relative to benzene

Overall emissions of toxic organic compounds were calculated and expressed as benzene equivalents, due to its known harmful effects in human health (Bird et al., 2005) and its higher inhalation unit risk value compared to other hazardous air pollutants with significant emission rates shown in Table 1. Inhalation Unit Risk (IUR) values or Unit Risk Estimates (URE) have been used to estimate the probability of contracting cancer; these parameters are considered as the upper-bound excess cancer risk estimated to result from a lifetime of continuous exposure to an agent at a concentration of 1 $\mu g\ m^{-3}$ in

Table 2
Emission rates of analyzed PAH compounds present in the exhaust of an agricultural tractor without after-treatment devices operating on petroleum diesel fuel and biodiesel blends with their respective inhalation unit risk values.

Species	Inhalation unit risk $(\mu g\ m^{-3})^{-1}$	Range of emission rates measured $(\mu g\ kg^{-1}\ CO_2)$
Anthracene	na	7–90
Phenanthrene	na	60–1600
Pyrene	na	25–170
Fluoranthene	na	30–60
Benzo(ghi)fluoranthene	na	5–10
Cyclopenta(cd)pyrene	na	<10
Benz(a)anthracene	1.10*E*-04	<10
Chrysene	1.10*E*-05	5–15
1-Methylchrysene	na	<2
Benzo(a)pyrene	1.10*E*-03	<5
Benzo(b)fluoranthene	1.10*E*-04	<10
Benzo(e)pyrene	na	<7
Benzo(k)fluoranthene	1.10*E*-04	<2
Perylene	na	<5
Benzo(ghi)perylene	na	<5
Indeno(1,2,3-cd)pyrene	1.10*E*-04	<5
Dibenz(ah)anthracene	1.20*E*-03	<10
Picene	na	<7
Coronene	na	<7

na: Values not available in OEHHA/ARB Risk Assessment Values list.
Particle phase PAH samples were analyzed from Quartz Fiber Filters and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS).
Gas phase PAH samples were analyzed from PUF: Polyurethane Foam filters with XAD resin by Gas Chromatography/Mass Spectrometry (GC/MS). See text for details.

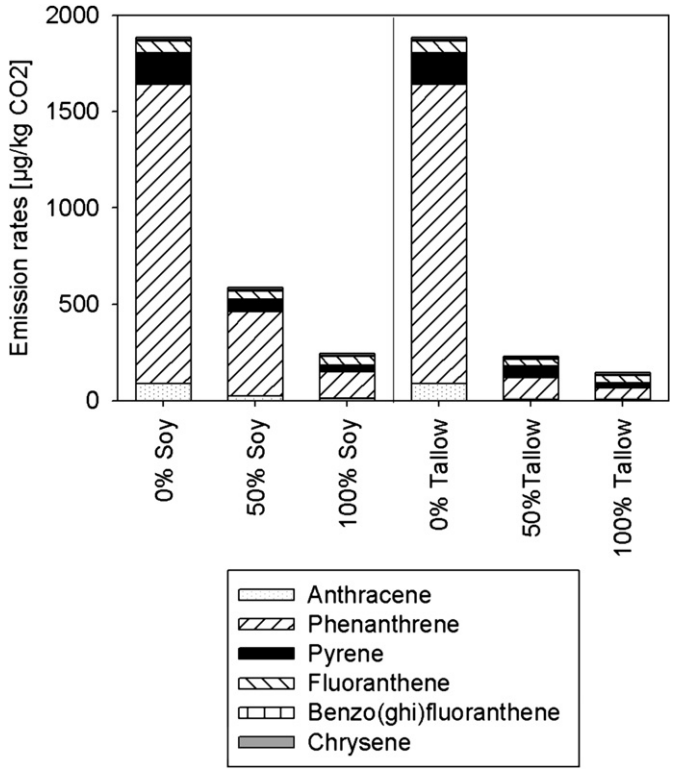

Fig. 4. Emission rates of analyzed particle and gas phase polycyclic aromatic hydrocarbons for different blends of petroleum diesel fuel and soybean oil and beef tallow based biodiesel in an agricultural tractor without exhaust after-treatment devices.

air (EPA, 2002). The URE values used in this study were taken from the list reported by the Office of Environmental Health Hazard Assessment (OEHHA) of the State of California (OEHHA, 2007). This list served as base for the Multiple Air Toxics Exposure Study III (MATES III), a monitoring and evaluation study conducted in the South Coast Air Basin (the continuation of previous air toxics studies part of the South Coast Air Quality Management District (SCAQMD)) (SCAQMD, 2008). The URE values were determined from studies on animal and cell culture exposure to diesel exhaust (Valberg and Watson, 1996). The available UREs for the species included in this study are shown in Tables 1 and 2 in units of $(\mu g\ m^{-3})^{-1}$. Emissions of toxic organics were calculated with the equation:

$$\text{Benzene relative emission of air toxic} = \text{Air toxic emmission rate} \times \left(\frac{\text{URE}_{\text{Benzene}}}{\text{URE}_{\text{Air toxic}}}\right)$$

Calculated emissions give an estimate of the toxicity associated with exposure to exhaust of petroleum diesel and biodiesel fuels. These emission rates are reported in units of mg Benzene/kg CO_2, as shown in Table 3. Fig. 5 shows formaldehyde and acetaldehyde with the highest toxic emissions followed by ethylbenzene and benzene. Since emission rates of PAHs were significantly lower compared to the other species included in Fig. 5, toxic emissions expressed as benzene equivalents were not calculated for these species. Blending petroleum diesel fuel with biodiesel results in reductions in toxic emissions of formaldehyde of 23% for B50, 42% for B100 and 40% for B100T; reductions in toxic emissions of acetaldehyde of 34% for B50, 53% for B100 and 42% for B100T compared to B0. Toxic emissions of the less dominant species ethylbenzene reduced by nearly 100% for B50, B100 and B100T compared to B0. From these results it can be concluded that blending petroleum diesel fuel with biodiesel reduces the health risk associated with the exposure to hazardous air pollutants present in the exhaust of a nonroad heavy-duty vehicle.

4. Conclusions

Results showed that emission rates of the detected hazardous air pollutant organic species decrease with increasing content of biodiesel in fuel blends for a nonroad vehicle without after-treatment devices. The largest reductions were shown for 2,2,4-trimethylpentane, toluene, ethylbenzene, *m*-, *p*- and *o*-xylene, and selected PAHs compared to other detected compounds, followed by benzene and carbonyl species formaldehyde and acetaldehyde showing reductions lower than 50%. Peng et al. found decreases in carbonyl emissions from a diesel engine operating on 20% waste cooking oil biodiesel blends compared to straight petroleum diesel fuel; these decreases were attributed to the higher oxygen content, higher cetane number and higher lubricity of B20 in comparison with diesel fuel, which leads to more complete combustion and increasing engine performance. Emission tests were performed under the US transient cycle protocol at several different cumulative mileages. The engine tested in this study was a Mitsubishi 4M40-2AT1, commonly used in pick-up trucks. The authors did not specify whether the engine had or not any exhaust after-treatment device. (Peng et al., 2008). On the other hand, Correa et al. found increases in carbonyl emissions from a diesel engine without after-treatment controls commonly used in urban buses in Brazil, operating on blends of 2, 5, 10 and 20% castor oil biodiesel. The increase in carbonyl emissions was attributed to the higher oxygen content due to the presence of ester molecules. This engine was tested under steady state conditions at different RPMs, in order to improve the test repeatability instead of mimicking real driving conditions (Correa and Arbilla, 2008). Results of a study on a diesel engine commonly used to power trucks in China, operating on pure soybean oil biodiesel and pure diesel fuel by He et al. agreed with the results of Correa et al. showing increases in carbonyl emissions for pure biodiesel fuel. In this case the engine without any after-treatment device was tested on the ISO 8178 Type C18-mode

Table 3
Emission rates of toxic organic compounds as benzene equivalents in the exhaust of an agricultural tractor without after-treatment devices operating on petroleum diesel fuel and biodiesel blends.

Air toxic	Emissions rates of air toxics expressed as emissions of benzene that yields an equivalent risk (mg Benzene per kg of CO_2)							
	B0	Contribution (%)	B50	Contribution (%)	B100	Contribution (%)	B100T	Contribution (%)
Benzene	12.10	1	5.58	1	6.10	1	3.99	1
Ethylbenzene	112	11	1.39	0	1.33	0	1.35	0
Formaldehyde	557	56	429	67	324	68	336	65
Acetaldehyde	308	31	205	32	146	31	179	34
Chrysene	0.040	0	0.018	0	0.014	0	0.013	0
Total	989		641		477		520	

B0: Pure diesel fuel; B50: 50% soy biodiesel; B100: Pure soy biodiesel; B100T: Pure tallow biodiesel.

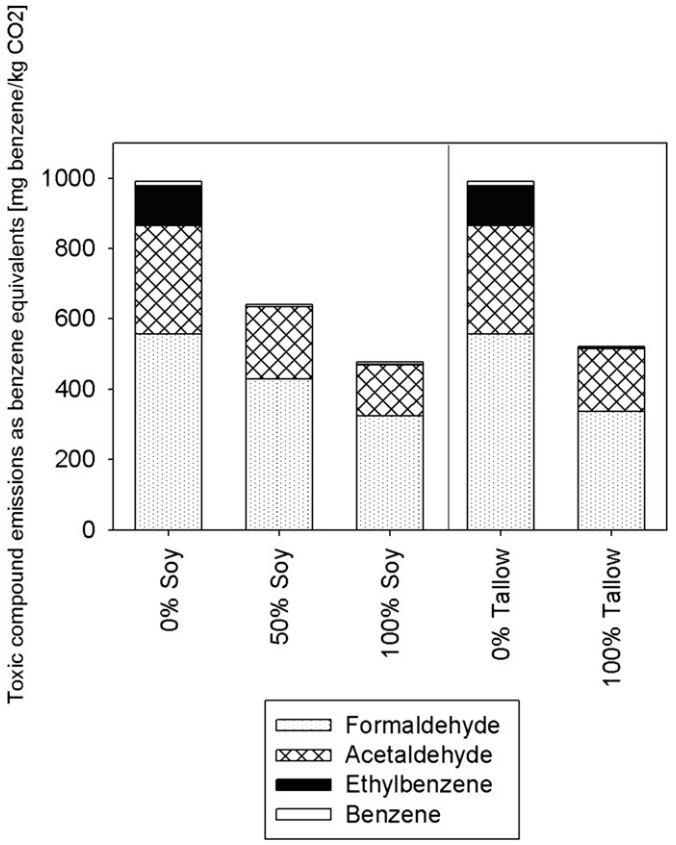

Fig. 5. Emission of analyzed toxic organic compounds with available inhalation unit risk value (OEHHA/ARB risk assessment values) as benzene equivalents for different blends of petroleum diesel fuel and soybean oil and beef tallow based biodiesel in an agricultural tractor without exhaust after-treatment devices.

steady state cycle at different load modes. The increase in carbonyl emissions was attributed to the higher oxygen content in biodiesel and incomplete combustion conditions, favored at higher load conditions. This study also makes an interesting comparison between the results of several other studies on carbonyl emissions of diesel engines operating on biodiesel blends concluding that the variation of carbonyl emissions of biodiesel-fueled engine can be affected by several factors, such as test engine level, biodiesel component and test cycle (He et al., 2009). Based on the above, and since this study has few comparable conditions with prior studies, such as engine type and test cycle, further research is required before reaching any conclusions about the causes of the slight decreases in carbonyl emissions for higher contents of biodiesel in fuel blends. Furthermore, since John Deere does not make onroad vehicles, the scope of this study should be limited to nonroad vehicles. Nevertheless, the engine used in the tractor tested in this study has been used in different nonroad vehicles other than agricultural tractors such as frontend loaders and graders also manufactured by John Deere and widely used in construction applications. In this sense, the reach of this study could be extended to such vehicles, keeping in mind the limitations associated with the impact associated with the different test cycles in emission profiles.

Emissions of toxic organic compounds expressed as benzene equivalents allows the estimation of relative toxicity associated with exposure to exhaust of an agricultural tractor without after-treatment devices operating on petroleum diesel and biodiesel fuels. Agricultural workers are commonly exposed to diesel exhaust, solvents, wielding fumes, pesticides, and other toxic substances used for several agricultural activities such as crop production, equipment repair, maintenance, and transportation (Hoppin et al., 2004). From these group, agricultural tractor drivers are additionally exposed to higher noise levels (Durgut and Celen, 2004), and constant vibration and postural stress which may lead to low back disorders (Bovenzi and Betta, 1994). Nevertheless, exposure to diesel exhaust still presents the higher health risk for agricultural tractor drivers (Hoppin et al., 2004). In year 1950, there were about 0.005 tractors per hectare of agricultural land at global level. By year 1970, this number increased to 0.012 tractors per hectare; and by year 2000, to 0.018, for a total increase of 70% in 50 years. At the same time, in 1950 there were 0.002 tractors per agricultural worker; by 1970 this number increased to 0.017; and in 2000–0.020 tractors per worker, indicating an increase of 90% in people exposed to the risks associated with the use of these vehicles (Federico, 2005). Considering this increasing global trend, operating agricultural tractors on biodiesel blends would significantly decrease the risk of developing cancer for drivers since emissions of toxic species formaldehyde, acetaldehyde and ethylbenzene decrease with increasing contents of soybean and beef tallow biodiesel in the fuel blends.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2011.12.007.

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